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(54) Title: MALEIMIDE MODIFIED POLYPROPYLENE IMINE DENDRIMERS AND A PROCESS FOR THEIR PREPARATION

(57) Abstract: The object of the invention is poly(propylene imine) type dendrimers, which have been modified by the help of the maleimide modification reaction with the amine groups in the shell of the dendrimer, and a method for manufacturing said dendrimers. Maleimide modified poly(propylene imine) dendrimers can be used as crosslinking agents, in coatings, adhesives and as matrix material in composites. It is characteristic to maleimide modified poly(propylene imine) dendrimer that the shell layer of it comprises reactive maleimide rings.

MALEIMIDE MODIFIED POLYPROPYLENE IMINE DENDRIMERS AND A PROCESS FOR THEIR PREPARATION

The invention relates to poly(propylene imine) type dendrimers, which have been modified by means of a maleimide modification reaction with the amine groups situated in the shell of the dendrimer, and a method for manufacturing the mentioned dendrimers. Maleimide modified poly(propylene imine) dendrimers can be used as crosslinking agents, in coatings, adhesives and as a matrix material in composites.

Treelike macromolecules with a highly branched structure and with a spherical shape constitute a family of polymers, which has been increasingly studied during recent years. These macromolecules having three-dimensional molecular architecture are referred to as dendritic polymers or dendrimers. Dendrimers differ significantly from conventional linear oligomers and polymers. Linear oligomers, which have sufficient molecular weight in order to be used e.g. in crosslinkable polyester resins, usually contain molecular chains with only two terminal functional groups in each molecule, while the structure of dendrimers is a compact spherical molecule with many branches which carry a high number of terminal functional groups on each molecule. The unique physical and chemical properties of dendrimers yields the compounds and products made from them interesting and special properties, as an example of them can be mentioned the exceptional and favourable rheological properties polyesters, such as low viscosity, when compared with linear oligomers. Dendrimers are usually manufactured by iterative synthesis in cycles, when in each stage the chemical and physical properties of the molecule, such as size, shape, reactivity and solubility, can be adjusted. Oligomers with a strongly branched structure can be used in many applications, such as catalysts, in pharmaceutical industry, as carriers for drugs, in cosmetics industry, adhesives, coatings, composites, agricultural chemicals and as multifunctional crosslinking agents.

A series of hyperbranched (meth)acrylated polyesters with different number of terminal double bonds per molecule has been presented and methods for the manufacture thereof have been disclosed in the patent application WO 96/07688. This

publication discloses a hyperbranched polyester of a polyol with 3 to 10 reactive hydroxyl groups and an aromatic polycarboxylic anhydride with 2 to 4 carboxyl groups, each hydroxyl group of the polyol forming an ester linkage with one anhydride group of the polycarboxylic anhydride, and further glycidyl (meth)acrylate or allyl glycidyl ether forming ester linkages with the remaining carboxyl groups of the anhydride and free hydroxyl groups. Further, in the hyperbranched polyester, (meth)acrylic anhydride and/or an aliphatic carboxylic anhydride form ester linkages with free hydroxyl groups. The said hyperbranched polyesters can be used as resins which are curable by UV-radiation.

It is known to manufacture amine terminated dendrimers by using diaminobutane as a core molecule, to the primary amine groups of which two equivalent acrylonitriles (reaction A) are added by Michael-addition reaction, after which the catalytic reduction of nitrile groups to primary amine groups is made (reaction B), when the result is a dendrimer od the first generation having four primary amine terminal groups. After this, the reaction series (A) and (B) is repeated 1 to 4 times, when finally a fifth generation molecule having amine terminal groups, is obtained. These poly(propylene imine) dendrimers are commercially available, Astramol (DSM), in different generations and having amine terminal groups or nitrile terminated groups.

Polyimide based thermosetting resins have achieved great favour in the industry because of their many advantageous properties, especially their good physical properties in elevated temperatures and wet environment. The use of maleimide, especially bismaleimides, in thermosetting resins is known. Maleimide is a versatile reactive group, which can react by different mechanisms, which is especially advantageous in the crosslinking of thermosetting resins. The chemical reaction between amino group and maleic acid anhydride is well known from the literature. Maleimides can be manufactured from primary amines and maleic anhydride in the presence of an organic solvent like dimethyl formamide, dimethyl acetamide, acetone, toluene, methylene chloride, tetrahydrofurane or comparable either by using heating or in the presence of acetic acid. Bismaleimides are highly reactive resins, which can be

croslinked in many ways. This is a consequence of the attractive character of two carbonyl groups of maleimide. Bismaleides polymerise easily without any catalyst when heating them over the melting point and as a result strongly crosslinked polymers with good thermal stability are achieved.

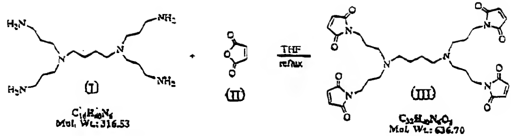
On the basis of what is said above it can be seen that there is an obvious need for macromolecules and especially oligomers, which have the exceptional properties of dendrimers, such as a compact spherical structure and numerous functional terminal groups, and the reactivitry of maleimides.

The object of the invention are reactive maleimide modified poly(propylene imine) dendrimers, a method to manufacture them and the usage of them.

Characteristics of the maleimide modified poly(propylene imine) dendrimers, of the method to manufacture them and of the usage of them are stated in the claims.

It has been found that according to the invention the above mentioned aims can be reached and the poly(propylene imine) type dendrimers can be customised especially to a crosslinkable thermosetting resin by making the maleimide modification reaction with the amine groups situated on the shell of the dendrimer. As a starting material for the dendrimers according to the invention can be used poly(propylene imine) dendrimers, which are commercially available having a tradename Astramol (DSM). It has been found that according to the invention branched multi-purpose maleimide modified poly(propylene imine) dendrimers can be manufactured to be used as starting materials for functionalised oligomeric and polymeric polyesters and polyamides according to the following figure 1.

Figure 1



Poly(propylene imine) dendrimer (I), which here is as an example a poly(propylene imine) dendrimer with four amine terminal groups, is let to react with maleic acid anhydride (II) in the presence of a solvent. After that the reaction mixture is heated up and the desired tetramaleimide is formed. In maleimide modification maleic acid anhydride reacts with the amine group forming a reactive maleimide ring.

According to the invention 5-50 mol%, favourably 10-20 mol% amount in excess 1. - 3. generation, favourably the first or the second generation poly(propylene imine) dendrimer, which has 4 or 8 amine terminal groups, is let to react with maleic acid anhydride in the presence of an inert solvent like tetrahydrofurane or methylene chloride at 20-40 °C temperature, after which the temperature is slowly elevated to 50-120 °C, favourably to 70-90 °C, and the mixing is continued. The crystallised product is separated by a suitable method, favourable it is filtered, washed up and dried.

In the shell layer of the maleimide modified poly(propylene imine) dendrimer there exist highly reactive maleimide rings, which are able to react using many different mechanisms. As examples from them can be mentioned the polymerisation by heat, by free radical polymerisation/crosslinking, when peroxides or azo compounds can be used as initiators, or by ion polymerisation using tertiary amides or imidazoles as catalysts or by copolymerisation with diene monomers and bisdienes.

Maleimide modified poly(propylene imide) dendrimers according to the invention can be used in numerous different applications, from which can be mentioned thermosetting plastics, coatings, inks, oil additives, adhesives, catalysts, composites and matrix materials for composites. The advantages of the dendrimers according to the invention are excellent reactivity, when they are especially good for multifunctional crosslinking agents, and a simple manufacturing method.

The following examples illustrate the compounds according to the invention and the method however not limiting the invention to them.

Example 1

Manufacture of tetramaleimide poly(propylene imine) dendrimer

Into a solution containing 1,0 g (3,2 mmol) of the first generation poly(propylene imine) dendrimer in 30 ml tetrahydrofurane, was added 20 mol% excess meaning 1,49 g (15,2 mmol) maleic acid anhydride in the room temperature. A white precipitate was immediately formed. After this the temperature was slowly increased to 70 °C and the mixture was agitated for 6 hours. The product was filtered and washed with a small amount of tetrahydrofurane and dried in a vacuum at 40 ° during the night, when tetramaleimide poly(propylene imine) dendrimer was obtained as white powder. The yield was 1,86 g (92 %).

^{1}H-NMR (C_5D_5N): α = 1,75 (m, 4H, $NCH_2CH_2CH_2CH_2N$), 2,02 (m, 8H, $NCH_2CH_2CH_2NR$), 2,84 (m, 4H, $NCH_2CH_2CH_2CH_2N$), 3,01 (t, 8H, $NCH_2CH_2CH_2NR$), 3,56 (m, 8H, $NCH_2CH_2CH_2NR$), 6,66 (s, 2H, CHCH).

^{13}H-NMR (C_5D_5N): α = 24,09 $NCH_2CH_2CH_2CH_2N$), 25,78 ($NCH_2CH_2CH_2NR$), 38,07 ($NCH_2CH_2CH_2NR$), 51,56 ($NCH_2CH_2CH_2NR$), 53,78 ($NCH_2CH_2CH_2CH_2N$), 167,32X169,64 (NCOCHCHCON).

Claims

1. Maleimide modified poly(propylene imine) dendrimer, characterised in that the shell layer comprises reactive maleimide rings.

2. Maleimide modified poly(propylene imine) dendrimer according to claim 1, characterised in that the dendrimer comprises a poly(propylene imine) dendrimer of 1.-3. generation, the amine groups of which have reacted with maleic acid anhydride forming maleimide rings to the shell layer.

3. A method for manufacturing maleimide modified poly(propylene imine) dendrimer characterised in that a 1. - 3. generation poly(propylene imine) dendrimer is let to react with maleic acid anhydride in the presence of a solvent, after which temperature in elevated and the maleimide modified poly(propylene imine) dendrimer obtained as the product is isolated, favourably filtered.

4. A method according to claim 3 characterised in that the poly(propylene imine) dendrimer is a dendrimer of 1. or 2. generation having 4 or 8 amine terminal groups.

5. A method according to claim 3 or 4 characterised in that the solvent is an inert solvent, favourably tetrahydrofurane or methylene chloride.

6. A method according to any of claims 3-5 characterised in that the reaction temperature is first 20-40 °C, after that the temperature is elevated to 50-120 °C , favourably to 70-90 °C.

7. The use of maleimide modified poly(propylene imide dendrimers as reactive crosslinking agents, in thermosetting polymers, coatings, inks, oil additives, adhesives, catalysts, composites and matrix materials for composites.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 00/00984

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08G 73/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, A 11-158123, (TOYO INK MFG CO LTD), 15 June 1999 (15.06.1999) & JP, 11-158123; 15 June 1999 (15.06.99); Abstract; Claims. --	1-7
A	US 4938885 A (CYRIL A. MIGDAL), 3 July 1990 (03.07.90), column 2, line 41 - line 45, abstract --	1-7
A	WO 9732571 A (HYPERION CATALYSIS INTERNATIONAL, INC.), 12 Sept 1997 (12.09.97), page 8, line 18 - line 33; page 10, line 29 - page 12, line 5; page 45, line 15 - line 26, abstract, Claims -- --------	1-6

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4938885 A	03/07/90	NONE	
WO 9732571 A	12/09/97	AU 724277 B	14/09/00
		AU 2197997 A	22/09/97
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		CA 2247820 A	12/09/97
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		EP 0910340 A	28/04/99
		IL 125987 D	00/00/00